

(13)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 450 674 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 91200406.6

(51) Int. Cl.⁵: C01G 25/02

(22) Date of filing: 26.02.91

(30) Priority: 02.03.90 IT 1953690

(43) Date of publication of application:
09.10.91 Bulletin 91/41(54) Designated Contracting States:
AT BE CH DE DK ES FR GB GR LI LU NL SE(71) Applicant: ENIRICERCHE S.p.A.
Corso Venezia 16
I-20121 Milan(IT)(72) Inventor: Castellano, Maurizio
Via Timermans 17/15
I-10146 Turin(IT)
Inventor: Lockhart, Thomas Paul
Via Europa, 30
I-20097 San Donato Milanese, Milan(IT)(74) Representative: Roggero, Sergio et al
Ing. Barzanò & Zanardo Milano S.p.A. Via
Borgonuovo 10
I-20121 Milano(IT)(54) **Process for preparing mixed oxides of zirconium and yttrium.**

(5) Mixed oxides of zirconium and yttrium [$ZrO_2(Y_2O_3)$], with an yttrium content (as computed as elemental metal) comprised within the range of from about 15 to about 21% by weight, as spherical particles with size comprised within the range of from 0.1 to 2 μm , with an average size of the particles lower than 1 μm , in the cubic crystal form, are obtained by:

- preparing a mixture by starting from an aqueous solution of zirconium and yttrium carboxylates; an organic solvent selected from the group consisting of nitriles or alcohols; and a non-ionic surfactant;
- causing solid colloidal particles of the precursor of mixed zirconium/yttrium oxides to precipitate from said mixture, by operating at a pH value comprised within the range of from 5 to 7, at room temperature or at temperatures close to room temperature; and
- calcining said precipitate of solid particles at a high temperature to cause said solid particles to be directly converted from the amorphous state into the cubic crystal form.

According to a particular form of practical embodiment, ultrasounds are applied to the mixture during said precipitation step, to further reduce the size of the precipitated particles.

The so obtained mixed oxides of zirconium and yttrium are suitable for use in the electronic sector, in particular as a solid electrolyte for fuel flow cells.

The present invention relates to a process for preparing the mixed oxides of zirconium and yttrium, suitable for use in the electronic sector, in particular as a solid electrolyte for fuel-flow cells.

Several mixed metal oxides are used in the electronic and mechanical sectors. An example thereof is zirconium dioxide (ZrO_2), which is stabilized in either of two crystal forms, as a function of the amount of yttrium oxide (Y_2O_3) incorporated inside it. In particular, it is well-known that in the mixed oxide, at a level of approximately 4 mol % of yttrium oxide, the tetragonal phase of zirconium dioxide is stabilized — which shows an extremely good mechanical stability; whereas at levels higher than 8 mol %, the cubic form, displaying interesting characteristics for application as the electrolyte in fuel-flow cells, is stabilized.

For the latter application, metal oxides in the form of spherical particles with a size as uniform as possible and of the order of one micron or less, are required.

According to the technique known from the prior art, metal oxides constituted by particles with submicronic size can be obtained by precipitation from homogeneous solutions of the inorganic salts of metals, as described, e.g., by E. Matijevic, *Acc. Chem. Res.* (1981) 14, 22; in U.S. patent No. 4,649,037 and in Japanese patent application No. 59-069,471. Another route known from the prior art is based on sol/gel reactions from organometallic precursors, such as described, e.g., by P. Colomban, in *L'Industrie Céramique* (1985), N. 792, 186.

Still another route is based on reactions of precipitations from emulsions, as described by A.B. Hardy in "Preparation of Submicrometer Unagglomerated Oxide Particles by Reaction of Emulsion Droplets", Ph. D. Thesis, Massachusetts Institute of Technology, Cambridge, MA (1988); M. Akins in "Preparation of Fine Oxide Powders by Emulsion Precipitation", Ph. D. Thesis, Iowa State University, Des Moines, Iowa (1987); and G. Gowda et al. in "Ceramic Powder from Sol-Emulsion-Gel Techniques", Final Project Report (R10), Am. Cer. Soc. Basic Science: Electronics and Glass Divisions Joint Meeting, New Orleans (LA), November 1986.

However, these approaches known from the prior art did not prove satisfactory owing to at least one of the following aspects: incapability to produce mixed oxides as particles with spherical shape and constant morphology, incapability or difficulty of reproducibility of the preparation method, and use of expensive reactants, such as, e.g., metal alkoxides.

The present Applicant has found now a simple and economically advantageous process which enables mixed oxides of zirconium and yttrium to be obtained in the cubic crystal form, as spherical particles with average size smaller than 1 μm , and with well-reproducible morphological characteristics.

In accordance therewith, the present invention relates to a process for preparing mixed oxides of zirconium and yttrium [$ZrO_2(Y_2O_3)$], with an yttrium content (computed as elemental metal) comprised within the range of from about 15 to about 21% by weight, as spherical particles with size comprised within the range of from 0.1 to 2 μm , with an average size of the particles lower than 1 μm , in the cubic crystal form, characterized in that:

- a mixture is prepared by starting from an aqueous solution of zirconium and yttrium carboxylates; an organic solvent selected from the group consisting of the aliphatic nitriles containing from 1 to 3 carbon atoms in their alkyl moiety, and of the aliphatic alcohols containing from 8 to 11 carbon atoms in their molecule; and a non-ionic surfactant;
- the precipitation is caused to take place from said mixture, of solid colloidal particles of the precursors of mixed zirconium/yttrium oxides by operating at a pH value comprised within the range of from 5 to 7, at room temperature or at temperatures close to room temperature; and
- said precipitate of solid particles is calcined at a high temperature to cause said solid particles to be directly converted from the amorphous state into the cubic crystal form.

Yttrium and zirconium carboxylates suitable for the intended purpose preferably are the salts of lower aliphatic carboxy acids, in particular zirconium and yttrium acetates.

The organic solvents are preferably selected from among acetonitrile and n-octanol.

The non-ionic surfactants are preferably selected from among the ethoxylated aliphatic alcohols having from 8 to 12 carbon atoms in their alkyl moiety and from 4 to 8 condensed units of ethylene oxide in their ethoxy portion.

When an aliphatic alcohol containing in its molecule from 8 to 11 carbon atoms is used as the organic solvent, a water-in-oil (W/O) emulsion is formed. When an aliphatic nitrile containing from 1 to 3 carbon atoms in its alkyl moiety is used for the same purpose, a single-phase mixture is obtained.

It should be observed that the combined use of the nitrile or alcohol solvent and of the non-ionic surfactant is critical in the process according to the present invention. In fact, when the process is carried out in the absence of these solvents or of the surfactant, or is carried out with different solvents, useful results are not obtained. In particular, when the process is carried out in an aqueous medium containing the surfactant and the metal carboxylates, but not containing the nitrile or alcohol solvent, no spherical particles

-- and not even of submicronic size -- of the mixed oxides of zirconium and yttrium are not obtained.

The either single-phase or double-phase mixture will preferably contain from 63 to 81% by weight of organic solvent, from 6 to 20% by weight of water and from 10 to 13% by weight of non-ionic surfactant. Furthermore, the aqueous phase will preferably contain from 5 to 10% by weight of yttrium and zirconium carboxylates, with a mutual molar ratio comprised within the range of from 0.6:1 to 2:1, and preferably of from 0.8:1 to 1.3:1.

The reaction of precipitation is carried out by keeping the mixture with stirring and operating within a range of pH values of from 5 to 7. If either required or advantageous, the own pH value typical of the aqueous solution of the carboxylates of zirconium and yttrium may be adjusted by the addition of small amounts of an either organic or inorganic base. Suitable bases for the intended purpose are alkali metal hydroxides, such as sodium hydroxide, and such aliphatic amines as butylamine. The amount of added base will be suitably comprised within the range of from 0 to 6×10^{-3} mol per each 1,000 g of mixture in case of alkali metal hydroxides, and of from 0 to 0.4 mol per each 1,000 g of mixture in case of aliphatic amines.

In the practicing of the process of the present invention, one of the following modalities can be selected;

- when the process is carried out in the absence of added bases, the process is advantageously performed by preparing an aqueous solution of yttrium and zirconium carboxylates and a solution of the surfactant in the selected organic solvent; both solutions are then brought into contact with each other with stirring, to form the mixture;
- when the process is carried out with an added organic base, the process is advantageously carried out by preparing a first mixture consisting of the organic solvent, the surfactant and the aqueous solution of zirconium and yttrium carboxylates and a second aqueous mixture consisting of the organic solvent, the surfactant and the aqueous solution of the inorganic base; said mixtures are then mixed with each other;
- when the process is carried out with the addition of an organic base, the process is advantageously carried out by preparing a mixture consisting of the organic solvent, the surfactant and the aqueous solution of zirconium and yttrium carboxylates and adding a solution of the organic base in the organic solvent.

In any case, by operating under the above reported conditions, with stirring and at a temperature comprised within the range of from about 18 °C to about 25 °C, a precipitate of the precursors of the mixed oxides is formed within a short time period, usually of the order of from 1 to 60 minutes. This precipitate is homogeneous, amorphous and is in the form of a powder consisting of spherical particles.

According to a form of practical embodiment of the present invention, the mixture from which the precipitate is being formed is submitted to the action of ultrasounds (sonication). In this case, a precipitate with still more reduced particle size is obtained.

When the precipitation is complete, the powder is separated from the mixture by such normal separation means as filtration and centrifugation. The powder is subsequently washed with alcohol, e.g., with ethanol at 95% and then bidistilled water, and is eventually dried. The dried powder is then calcined at high temperatures, typically of from about 900 °C to about 1,400 °C, for a time of the order of from 1 to 10 hours. Under these conditions, the direct transformation of the cubic crystal form of zirconium stabilized with yttrium oxide is directly achieved, with the morphological characteristics of the precipitated powder being retained.

In particular, the amount of yttrium (evaluated as metal) in the calcined product may reach values as high as 21% by weight, and typically is comprised within the range of from about 10 to about 21% by weight. The particles of the calcined powder are of spherical shape, with size comprised within the range of from 0.1 to 2 µm, and with an average size smaller than 1 µm.

Therefore, the process according to the present invention enables powders to be produced with constant morphology, of mixed zirconium and yttrium oxides, or -- said in an equivalent way -- of zirconium oxide doped with yttrium, by a simple and economically favourable reaction. This process makes it possible said oxides to be obtained in the form of particles of spherical shape, which retain their morphological features even after calcination.

The reactants used, and, in particular, zirconium and yttrium acetates, are cheap reactants. The yields of precursor, i.e., of product obtained from the precipitation, are high, and in particular of from 90 to 100%, as computed relatively to zirconium.

Advantageously, the reaction of precipitation takes place at room temperature. It requires very short reaction times, and makes it possible very large amounts of yttrium to be homogeneously incorporated in the precipitate, as set forth above.

This precipitate is directly transformed by calcination into the cubic crystal form of stabilized zirconium

dioxide, which cubic crystal form is particularly useful if the product has to be employed for electrodes for fuel-flow cells.

The following experimental examples are reported to better illustrate the present invention.

5 Example 1

An amount of 21 g is prepared of a first mixture containing 15 g of acetonitrile, 3 g of the surfactant commonly available from the market Brij 30 (adduct of dodecanol with an average of 4 mol of ethylene oxide added) and 3 g of aqueous, 0.2 M sodium hydroxide.

10 This mixture is added, with stirring, to a cylindrical vessel containing 24 g of a second mixture consisting of 15 g of acetonitrile, 3 g of Brij 30 and 6 g of an aqueous solution at 2.5% by weight of zirconium acetate and 2.5% by weight of yttrium acetate. The molar ratio of yttrium to zirconium results hence to be equal to 1.23:1. By operating at room temperature (20-25 °C), within a time of 5 minutes of the mixing, a white precipitate is formed, which is a powder constituted by particles with spherical shape. The
15 reaction mass is kept stirred for 1 hour. The precipitate obtained is separated, is washed firstly with ethanol at 95%, and then with bidistilled water. The washed precipitate is dried at 60 °C for 12 hours in air, and 0.116 g of dried solid product is obtained.

The analysis carried out by electron microscopy indicates that the product is a powder with spherical morphology. The weight loss on calcination at 1,200 °C for 5 hours is of 33.5%. The analyses carried out by
20 atomic absorption on the calcined product show the presence of 20.8% by weight of yttrium, and 52.3% by weight of zirconium. The yield, computed on the zirconium contained in the starting material, is of 93%. The calcined powder consists of particles with size comprised within the range of from 0.2 to 2 µm, and with an average size of less than 1 µm.

25 Example 2

The process is carried out as in Example 1, with a first mixture consisting of 27.7 of acetonitrile, 5.54 g of Brij 30 and 2.77 g of aqueous, 0.2 M sodium hydroxide being mixed with a second mixture consisting of
30 30 g of acetonitrile, 6 g of Brij 30 and 12 g of an aqueous solution at 2.5% by weight of yttrium acetate and 2.5% by weight of zirconium acetate. Also in this case, the molar ratio of yttrium to zirconium is of 1.23:1.

Operating as in Example 1, after drying 0.503 g is collected of a solid product which is calcined for 5 hours at 1,200 °C, during which time it undergoes a weight loss of 35%.

The elemental analysis shows that the mixed oxide obtained as the end product contains 15 mol % of Y_2O_3 and 85 mol % of ZrO_2 . This composition is confirmed by the analysis of the cell parameters, obtained by X-ray diffraction, which shows that the product is composed by 13.5 mol % of Y_2O_3 and 86.5
35 mol % of ZrO_2 , securing a cubic crystal form of the calcined material.

Example 3

40 By operating as in Example 1, two mixtures are blended. The first mixture is composed by 2 g of aqueous, 0.2 M NaOH, 5 g of Brij 30 and 25 g of n-octanol, and the second mixture consists of 0.5 g of yttrium acetate at 5% by weight in water and 0.5 g of zirconium acetate at 5% by weight in water, 1 g of Brij 30 and 5 g of n-octanol.

A white-coloured, milky emulsion is obtained which, within 5 minutes, produces a colloidal, white-
45 coloured precipitate consisting of particles of from 0.1 to 2 µm of size. The reaction mixture is kept stirred for about 10 minutes, then the precipitate is separated, is washed with ethanol at 95% and then bidistilled water, and is finally dried at 60 °C for 12 hours.

Example 4

50 A single-phase mixture is prepared, which contains:

- * (1) freshly-distilled acetonitrile : 689.9 g;
- * (2) surfactant available from market Brij 30 : 137.3 g;
- 5 * (3) aqueous, 0.2 M sodium hydroxide : 33.3 g;
- * (4) zirconium acetate at 5% by weight in
water, filtered through an 0.2- μ m
10 membrane : 71.4 g;
- * (5) yttrium acetate at 5% by weight in
water, filtered through an 0.2- μ m
15 membrane : 71.4g.

The reactants (1), (2) and (3) are charged to a cylindrical reactor in the order shown, with stirring. A solution is obtained, to which the reactants (4) and (5) are added from a charging funnel, with a milky mixture being produced. The reaction is allowed to proceed for a 33-minute time at 20°C, with stirring, and a white-coloured precipitate is formed, which is washed twice with ethanol at 95% and then with bidistilled water. The washed precipitate is dried at 60°C for 5 hours under vacuum and 3.11 g is obtained of a solid product.

The analysis by electron microscopy shows that the obtained powder is constituted by particles with spherical shape. The weigh loss on calcination at 1,200°C for 5 hours is of 34.4%. The analyses carried out by atomic absorption on the calcined product show that said product is constituted by 12.9% by weight of yttrium and 36.1% by weight of zirconium. The yield, computed relatively to the zirconium contained in the starting reactants, is of approximately 100%. The X-ray diffraction analysis confirms a cubic crystal form after calcination. The calcined powder consists of particles of from 0.2 to 2 μ m of size, with an average size smaller than 1 μ m.

Example 5

A mixture is prepared, which contains:

- * (1) 1-octanol (a Merck product) : 655.0 g;
- * (2) surfactant available from market Brij 30 : 131.0 g;
- 40 * (3) aqueous, 0.2 M sodium hydroxide : 43.0 g;
- * (4) zirconium acetate at 5% by weight in
water, filtered through an 0.2- μ m
45 membrane : 10.9 g;
- * (5) yttrium acetate at 5% by weight in
water, filtered through an 0.2- μ m
50 membrane : 10.9 g.

The reactants (1), (2) and (3) are charged to a reactor of cylindrical shape, in the order shown, with stirring. A cloudy, emulsified mixture is obtained, to which (4) and (5) are added, as one single combined solution, from a charging funnel, with a strongly milky emulsion being produced. The reaction is allowed to proceed for a 33-minute time at 20°C, with stirring, and a white-coloured precipitate is formed, which is washed twice with ethanol at 95%. The washed precipitate is dried at 60°C for 6 hours under vacuum and 0.71 g is obtained of a solid product.

The analysis by electron microscopy shows that the powder is constituted by particles with spherical shape. The weigh loss on calcination at 900 ° C for 5 hours is of 35%. The analyses carried out by atomic absorption on the calcined product shown that said product is constituted by 19.2% by weight of yttrium and 27.2% by weight of zirconium. The yield, computed relatively to zirconium contained in the starting reactants, is of approximately 100%. The X-ray diffraction analysis confirms that the obtained product has a cubic crystal structure after calcination. The calcined powder consists of particles of from 0.2 to 2 μm of size, with an average size smaller than 0.5 μm .

Claims

1. Process for preparing mixed oxides of zirconium and yttrium [$\text{ZrO}_2(\text{Y}_2\text{O}_3)$], with an yttrium content (computed as elemental metal) comprised within the range of from about 15 to about 21% by weight, as spherical particles with size comprised within the range of from 0.1 to 2 μm , with an average size of the particles lower than 1 μm , in the cubic crystal form, characterized in that:
 - a mixture is prepared by starting from an aqueous solution of zirconium and yttrium carboxylates; an organic solvent selected from the group consisting of the aliphatic nitriles containing from 1 to 3 carbon atoms in their alkyl moiety, and of the aliphatic alcohols containing from 8 to 11 carbon atoms in their molecule; and a non-ionic surfactant;
 - the precipitation is caused to take place from said mixture, of solid colloidal particles of the precursors of mixed zirconium/yttrium oxides by operating at a pH value comprised within the range of from 5 to 7, at room temperature or at temperatures close to room temperature; and
 - said precipitate of solid particles is calcined at a high temperature to cause said solid particles to be directly converted from the amorphous state into the cubic crystal form.
2. Process according to claim 1, characterized in that said yttrium and zirconium carboxylates are the salts of lower aliphatic carboxy acids and preferably are zirconium and yttrium acetates, the organic solvents are selected from acetonitrile and n-octanol and the non-ionic surfactants are selected from among the ethoxylated aliphatic alcohols containing from 8 to 12 carbon atoms in their alkyl moiety and from 4 to 8 condensed units of ethylene oxide in their ethoxy portion.
3. Process according to claim 1, characterized in that the mixture contains from 63 to 81% by weight of organic solvent, from 6 to 20% by weight of water and from 10 to 13% by weight of non-ionic surfactant, with the aqueous phase containing from 5 to 10% by weight of yttrium and zirconium carboxylates, with a mutual molar ratio comprised within the range of from 0.6:1 to 2:1, and preferably of from 0.8:1 to 1.3:1, and the precipitation being carried out at a temperature comprised within the range of from about 18 ° C to about 25 ° C, with the mixture being kept stirred for a time of from 1 to 60 minutes.
4. Process according to claim 1, characterized in that the value of pH of the aqueous solution of zirconium and yttrium carboxylates is adjusted by the addition of an alkali metal hydroxide and preferably sodium hydroxide, or of an aliphatic amine, and preferably butylamine, in an amount comprised within the range of from 0 to 6×10^{-3} mol per each 1,000 g of mixture in case of alkali metal hydroxides, and of from 0 to 0.4 mol per each 1,000 g of mixture in case of aliphatic amines.
5. Process according to claim 1, characterized in that the mixture from which the precipitate is formed, is submitted to the action of ultrasounds.
6. Process according to claim 1, characterized in that the calcination is carried out at a temperature of from about 900 ° C to about 1,400 ° C, for a time of the order of from 1 to 10 hours.



European
Patent Office

EUROPEAN SEARCH
REPORT

Application Number

EP 91 20 0406

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 310 480 (RHONE-POULENC CHIMIE) * Page 9 *	1	C 01 G 25/02
A	-----	2,4,6	
Y	EP-A-0 304 243 (ALCON INTERNATIONAL LTD) * Column 6; claims 1,2,4; column 2, lines 58-63 *	1	
A	EP-A-0 224 375 (MINNESOTA MINING) -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 01 G C 01 B

Place of search	Date of completion of search	Examiner
The Hague	10 June 91	LIBBERECHT-VERBEECK

CATEGORY OF CITED DOCUMENTS
X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons
&: member of the same patent family, corresponding document